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Desulfurization of Low Temperature Char  
I - Rate and Total Inhibition Data in Batch Systems

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INTRODUCTION

The desulfurization of char with hydrogen and hydrogen steam mixtures<sup>1)</sup> was described in a previous publication. The data were obtained in a batch system and the role of hydrogen sulfide in inhibiting the rate of the desulfurization process was discussed.

The char used in the earlier work was produced from a Pittsburgh Seam coal in the Disco process, a commercial rotary kiln, low temperature carbonization process. These data are now extended to chars produced from a number of other Pittsburgh Seam coals in a fifty ton per day fluidized low temperature carbonization pilot plant.

Data were obtained both in very shallow beds where the role of hydrogen sulfide inhibition is very small and also in deep batch beds where inhibition of the desulfurization rate is quite large.

It is well known from earlier work by Powell<sup>2)</sup> and Huff<sup>3)</sup> that the reaction of hydrogen sulfide-hydrogen mixtures with carbonaceous materials is reversible. High ratios of hydrogen-hydrogen sulfide cause sulfur removal from the chars while at low ratios sulfur is deposited on the chars. Powell<sup>2)</sup> showed that a characteristic isotherm could be developed for materials such as sugar char and coke by passing hydrogen very slowly over the material under investigation and measuring the hydrogen sulfide evolved.

Powell<sup>2)</sup>, however, showed that this was not a true equilibrium process since the isotherms depended to some extent on the prior thermal history and origin of the carbonaceous material.

We have developed similar isotherms by a different technique than was used by Powell for the low temperature chars used in this investigation. These isotherms were developed under conditions of time and temperature similar to those that would be employed in an actual desulfurization process. They, therefore, represent the hydrogen-hydrogen sulfide ratio as a function of the sulfur content of the char which corresponds to complete inhibition of the desulfurization process.

These total inhibition isotherms provide a useful tool for interpretation of the hydrogen sulfide inhibition observed in the present work as well as some of our earlier published data. They also provide a basis for estimation of the minimum hydrogen circulation requirements in possible commercial processes.

#### EXPERIMENTAL

##### Raw Materials

The chars used in this work were all produced in Consolidation Coals fifty ton per day fluidized low temperature carbonization pilot plant at 900-950°F. The coals from which the chars were prepared were all Pittsburgh Seam coals from three different mines. These were the Arkwright and Montour 10 mines of Consolidation Coal Company and the Alexander mine of the Valley Champ Coal Company. The sulfur content of the chars varied over the range of 1.3 to 4.5 weight percent. The analysis of the feed chars is given in Table I.

The investigations were of three types and were carried out in three different kinds of equipment and by three different procedures.

##### Total Inhibition Data

The method used by Powell in determining the total inhibition isotherms suffers from the major deficiency that there is no assurance that equilibrium was achieved.

The data reported here were obtained by a more standard equilibrium method. Chars of several sulfur contents were contacted with  $H_2S-H_2$  mixtures of several concentrations. Each run was of sufficient duration to obtain a reasonable approach to equilibrium.

A single series of experiments with a constant gas composition caused sulfiding of the lower sulfur chars and desulfurization of the higher sulfur chars. The sulfur content corresponding to total inhibition was thus bracketed by approaching it from both directions.

The chars employed for developing a particular isotherm covered a range of sulfur values. They were prepared by desulfurization of the standard nitrogen pretreated char with hydrogen. The pretreatment and desulfurization temperature were always the same as that for which the isotherm was developed.

The equipment used in this study is shown in Figure 1. The reactor was a 22 mm ID Vycor tube about 20" long with a standard taper joint at the upper end for the take-off tube and thermowell assembly.

A mixture of hydrogen sulfide and hydrogen was made up and stored in the gas mixture bomb. It was analyzed for hydrogen sulfide by passing a portion of it after drying with anhydrous through a Nesbit bottle containing Ascarite and measuring the volume of residual hydrogen passed. The hydrogen sulfide content was obtained from the weight gain of the Ascarite. The analysis was made before and after a run and the average used for the calculations.

A ten-gram char sample was used for an actual run. The Vycor reactor was brought up to temperature with nitrogen passing through the char

bed. The nitrogen was replaced with the hydrogen sulfide - hydrogen mixture after the temperature was lined out. The reactor was operated as a fluidized bed using a superficial velocity of 0.4 feet per second. The treatment of the char was continued generally for a period of from 2-4 hours. The residue char was analyzed for total and sulfide sulfur. The observed sulfur level of the char was then associated as near equilibrium with the gas composition used.

Total sulfur was determined by the Eschka<sup>4)</sup> method while sulfide sulfur was determined by the evolution<sup>4)</sup> method.

All the data obtained in runs of this type are not reproduced. The data from which the 1350°F isotherm is derived are given in Table II.

The isotherms at 1350°F developed from these data for the Arkwright and Alexander Mine chars are shown in Figure 2 while 1100 and 1600°F isotherms for Arkwright char are given in Figure 3. The experimental points shown are distinguished by arrows pointing to the left or right. The left arrow designates the lowest sulfur value reached in a series of desulfurization runs at the gas composition used. A right arrow similarly designates the highest sulfur value reached in a corresponding series of sulfiding experiments.

#### Deep Bed Runs

The procedure used in these runs was similar to that described in our earlier gasification<sup>5)</sup> and desulfurization<sup>1)</sup> studies. The main difference was the use of a 4-inch internal diameter pressure balanced reactor instead of the 1-1/2-inch diameter Uniloy reactor described previously<sup>5)</sup>.

All runs were made at 1600°F and 6 atmospheres pressure using 35-100 mesh Arkwright I char. The runs were made using a batch fluid bed fluidized with pure hydrogen at 0.2 ft. per second. The char was introduced into the reactor when the latter reached 950°F. The char was fluidized in nitrogen and preheated to 1600°F. The pretreatment in nitrogen was continued for one hour after 1600°F was reached. The reactor was pressurized to 6 atmospheres and the hydrogen turned on.

A series of 9 runs was made with hydrogen treatment times of 30, 60 and 120 minutes and initial bed weights of 430, 860 and 1720 grams.

The loss in bed weight and in sulfur due to the nitrogen pretreatment was determined by separate experiments. The average analysis of the pretreated Arkwright char is given in Table I.

No analyses other than proximate and ultimate of bed residues were made in this series of runs. Some typical analyses of the bed residues are given in Table III.

The complete summary of run conditions and of the sulfur analyses of the solid residues are given in Table IV.

#### Shallow Bed Runs

The aim of these runs was to obtain differential data, i.e., the rate of desulfurization in pure hydrogen and in the absence of any significant concentration of hydrogen sulfide.

The runs were made using a batch fluid bed. The 1-1/2-inch diameter Uniloy reactor system formerly employed was used in this work. The char bed was, however, contained in a stainless steel liner which was lifted out of the reactor at the end of each run.

One important change in procedure was made. The initial pretreatment used previously for one hour in nitrogen before desulfurization was eliminated. This was accomplished by preheating the reactor to desulfurization temperature in a hydrogen atmosphere before admitting the char. A ten-gram char sample was usually used although all the work with the Alexander char as well as some with the other chars was made with a five-gram sample. The weighed char sample was charged, the reactor sealed and brought to full pressure and temperature as quickly as possible. This process took between four to ten minutes. The small char bed was fluidized with hydrogen at a velocity of 0.4 feet per second for one hour after full pressure was reached. The reactor was quickly depressurized, purged with nitrogen and the bed residue removed cooled in nitrogen and recovered for weighing and analysis. The only analyses made were the sulfur content of the bed residues.

Three different chars of widely different sulfur content whose analyses are given in Table I were used in this work. Each char was treated at five different temperatures from 1000 to 1600°F inclusive and at three pressures, i.e., 1, 3 and 6 atmospheres absolute.

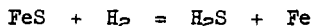
The total hydrogen used in these runs per lb. of char treated varied from about 140-280 SCF depending on whether a five or ten-gram bed was used in the runs at 1 atmosphere to about 600-1200 SCF in the six atmosphere runs. A pair of runs were made at 1450°F and 1600°F and 1 atmosphere where the hydrogen rate was increased by a factor of three, i.e., from about 140 to 400 SCF/lb. The sulfur content of the residue at 1450°F, i.e., 0.66 weight percent, was unaffected by this increase in hydrogen-char ratio while at 1600°F a decrease from 0.72 to 0.58 weight percent was noted. It is clear, therefore, that the data approaches that which would be obtained in a true differential reactor.

The sulfur levels of the treated chars are presented graphically in Figures 6, 7 and 8.

### Interpretation of Results

#### Total Inhibition Data

The data of Figures 2 and 3 show the position of the sulfide plateau in the correct place as reported by Powell<sup>2)</sup> and is in accord with the equilibrium data of Alcock and Richardson<sup>3)</sup>. The plateau corresponds to the equilibrium in the reduction of iron sulfide, i.e.,



The amount of organic sulfur "locked" below the sulfide plateau is also in general agreement with Powell's<sup>2)</sup> data for coke. No distinction can be made from our data, however, between the forms of organic sulfur as discussed by Powell, i.e., solid solution and adsorbed sulfur. The comparison between the data for Arkwright char and Alexander Mine char given in Figure 2 shows that in the latter case the curve does not go through the origin. The reason for this is that the Alexander char contains about 0.25 weight percent of sulfide sulfur in the form of calcium sulfide which is substantially irreducible.

The total inhibition data for the organic sulfur on a moisture and ash-free basis for Arkwright char is given in Figure 4. A comparison is also made with Powell's data for sugar char. It is seen that the inhibition of the organic sulfur removal like that of the sulfide sulfur becomes more marked as the temperature is lowered. Powell's data for sugar char is similar to that of the coal derived chars but is far from identical. It may thus be concluded that the total inhibition isotherms are not universal but depend on the nature of the char. The Alexander Mine data also show differences when plotted on a moisture and ash-free basis. The removal of the organic sulfur from this char appears to be more highly inhibited than removal from the Arkwright char. The data are not plotted, however, since the analytical data did not provide in this case as clear a distinction between the sulfide and organic sulfur.

#### Deep Bed Runs

Under conditions where the rate of desulfurization is rapid, the total inhibition isotherms conservatively determine the amount of desulfurization that can be achieved rather than the desulfurization kinetics. The result is conservative since the total inhibition isotherms are representative for chars that have received several hours of thermal pretreatment at the temperature in question. Powell's data as well as some of our own experience suggests that the sulfur is somewhat more labile in the raw char.

Consider, for example, desulfurization in an isothermal batch fluidized bed. In the limiting totally inhibited case, the gas leaving the bed will be in equilibrium with the solids in the bed at any instant. The equilibrium conditions may be developed mathematically in terms of the total inhibition isotherms by forcing a sulfur balance between the sulfur in the gas and in the solid. By this procedure we find

$$\int_0^{n_H} \frac{dn_H}{1 - \alpha n_H} = \int_S^{S_0} \frac{dS}{32f(S) - \alpha S} \quad 1)$$

$$\text{or} \quad \frac{1}{\alpha} \ln \left( \frac{1}{1 - \alpha n_H} \right) = \int_S^{S_0} \frac{dS}{32f(S) - \alpha S} \quad 2)$$

The quantities involved in equations 1) and 2) are defined in the appendix. Equation 2) may be further simplified if the devolatilization or loss in weight of the char due to passage of hydrogen through the bed can be neglected, i.e.,  $\alpha = 0$ . In this case equation 2) reduces to

$$n_H = \frac{1}{32} \int_S^{S_0} \frac{dS}{f(S)} \quad 3)$$

Where one is interested only in relatively high sulfur levels, i.e., above about 1.2-1.3 weight percent sulfur for the Arkwright case it is a sufficiently good approximation to treat  $f(s)$  as a linear function, i.e.,

$$f(s) = k(s - S_i) \quad (4)$$

Using equation 4) equations 2) and 3) reduce to the simplified equations 5) and 6) respectively

$$\log\left(\frac{1}{1 - \alpha n_H}\right) = \frac{\alpha}{(32k - \alpha)} \log\left[\frac{(32k - \alpha)S_0 - 32kS_i}{(32k - \alpha)S - 32kS_i}\right] \quad (5)$$

$$n_H = \frac{1}{32k} \ln\left(\frac{S_0 - S_i}{S - S_i}\right) \quad (6)$$

The above equations can be used to determine the "maximum" amount of desulfurization that can be achieved in batch fluidized beds. The first rather remarkable result worth noting is the rather high degree of desulfurization that was achieved in the batch desulfurization of the feed char. The desulfurization from 1.96 to 1.43 weight percent sulfur was accomplished simply by devolatilization in a stream of nitrogen at 1600°F. Results to be reported in a companion paper show that under these conditions the yield of devolatilized char is 88.7 weight percent of the feed char while the amount of hydrogen evolved is about 2.6 SCF per pound of feed char, i.e.,  $\alpha = 16.2$ . Based on the assumption that all of the hydrogen was evolved at 1600°F and using equation 5), one calculates that the sulfur content of the devolatilized char should be 1.35 weight percent as against the observed value of 1.43 weight percent. It is thus obvious that very close to equilibrium conditions are maintained during devolatilization of the char in spite of the very low average partial pressure of hydrogen. The extraordinary lability of the sulfur in low temperature char is thus emphasized.

The degree of desulfurization obtained is also clearly greater than is achieved in the devolatilization of coal in a coke oven. The reason for this can be traced again back to the total inhibition isotherm. The staging effect obtained by batch desulfurization in a fluidized bed is now absent since the coke sees on the average a gas corresponding in sulfur content to the whole coke oven gas. For example, if the Arkwright char were equilibrated with the whole devolatilization product gas the sulfur content of the product char would rise from 1.43 to 1.65 weight percent.

After the char is devolatilized, further weight loss in the hydrogen treatment in deep beds is rather minor. This is clear from the data given in Table IV. As a good approximation it is possible to assume  $\alpha = 0$  in

establishing the equilibrium desulfurization curves for devolatilized chars. It is also necessary to assume that the total inhibition isotherms are independent of the pressure. This assumption seems reasonable but has not been proven experimentally.

Curves which are shown in Figure 5 have thus been developed by application of equation 3) which show the minimum amount of hydrogen required for desulfurization of char in batch fluidized beds. Curves are shown for operation at both 1600°F and 1350°F.

The experimental data from the deep bed runs are shown for comparison. It is seen that for beds larger than 430 grams the results are determined largely by equilibrium and not by kinetics. This is true at least under the operating conditions used, i.e., 6 atmospheres pressure at 1600°F.

Some of our prior published data using hydrogen-steam mixtures for char desulfurization was treated in the same way. A comparison of the sulfur values observed with those calculated on the above equilibrium basis is given in Table V. The same results are apparent, i.e., at partial pressures of hydrogen above 1.5 atmospheres and for beds larger than 70 grams that the desulfurization is equilibrium controlled. The steam under these conditions thus plays the role of an inert diluent with respect to desulfurization.

#### Shallow Bed Runs

It is clear that for shallow char beds, kinetics and not equilibrium determines the amount of desulfurization. Thus, from Figure 5, it is clear that the hydrogen to char ratio used in our shallow bed runs, i.e., greater than 140 SCF per pound would be sufficient to achieve very much lower sulfur values than are apparent from the results shown in Figure 6.

All the results with the three different chars are plotted on a percentage sulfur elimination basis in Figure 9. It is thus seen that the sulfur elimination achieved in shallow beds, is as a first approximation, a function only of the conditions employed and independent of the sulfur content of the feed char.

The sulfur elimination shown is the percentage of the total sulfur in the feed char that is rejected and thus takes account of the measured weight loss of the chars during the desulfurization treatment.

The above correlation is consistent with the assumption that sulfur elimination is roughly a first order reaction independent of the sulfur level of the feed char, i.e.,

$$-\frac{dS}{dt} = k P_{H_2}^a S \quad 7)$$

Equation 7) in integrated form may be written

$$\ln\left(\frac{1}{1-S}\right) = k P_{H_2}^a t \quad 8)$$

Where  $\beta$  is the fraction sulfur eliminated. The data cannot be used to obtain reliable values of the rate constant  $k$  and the reaction order  $a$  since only one time was investigated. It is clear from the data, however, that the value of  $a$  is less than one, i.e., the reaction is less than first order with respect to hydrogen pressure.

# APPENDIX

## Definition of Mathematical Terms

$S_0$  = Initial Total Sulfur Content of Char Weight Percent.

$S$  = Final Sulfur Content of Char.

$S_i$  = Intercept for Linear Approximation  $f(s) = k(s - S_i)$

$M_A$  = Total Mols Hydrogen Sulfide in Gas x 100 Per Lb. Char Fed.

$n_H$  = Mols Hydrogen Passed Per Lb. Char.

$\alpha$  = Lbs. of Char Devolatilized Per Mol of Hydrogen Passed.

$f(s)$  = Total Inhibition Isotherm, i.e., Sulfur Content of Char Versus  $\frac{n_s}{n_H}$



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Table I

ANALYSIS OF FEED CHARs (DRY BASIS)

	<u>Arkwright I<sup>1)</sup></u>		Raw Arkwright II <sup>2)</sup>	Raw Montour 10	Raw Alexander Mine
	Raw	Pretreated <sup>3)</sup>			
H	2.99	0.68	3.22	3.34	3.25
C	77.69	84.70	78.29	80.46	70.46
N	1.74	1.27	1.72	1.79	1.25
O	4.93	0.68	5.01	6.56	5.89
S	1.96	1.43	2.53	1.33	4.51
Ash	10.69	11.24	9.23	6.52	14.64
Sulfide S	0.13	0.39	0.39	-	-

1) Feed char to deep bed desulfurization runs.

2) Feed char to shallow bed and total inhibition experiments.

3) Pretreated at 1600°F for one hour in nitrogen.

Table II

TABULATED DATA FOR CHAR-H<sub>2</sub>S REACTION AT 1350°F

All feeds were produced at 1350°F from Arkwright Char II

All runs made with 10 gms of char; gas rate was 1.2 SCFH

Run No.	Gas Comp. (% H <sub>2</sub> S in H <sub>2</sub> )	% Sulfur in Feed Char			% Sulfur in Residue Char			Time of Treatment
		Organic MAF	Sulfide Dry	Total Dry	Organic MAF	Sulfide Dry	Total Dry	
74	0.11	0.33	0.07	0.37	0.36	0.07	0.39	249 min
75	0.15	0.33	0.07	0.37	0.52	0.40	0.86	234
86	0.17	1.33	0.13	1.31	0.91	0.35	1.16	211
73	0.20	0.33	0.07	0.37	0.70	0.32	0.94	196
79	0.26	0.55	0.19	0.68	0.72	0.46	1.09	226
70	0.27	1.33	0.13	1.31	1.06	0.29	1.24	201
68	0.53	0.33	0.07	0.37	1.04	0.40	1.32	226
69	0.54	1.33	0.13	1.31	1.18	0.37	1.41	236
78	0.53	1.84	0.31	1.96	0.98	0.51	1.38	215
67	1.06	0.33	0.07	0.37	1.20	0.33	1.40	151
71	1.05	1.33	0.13	1.31	1.43	0.35	1.62	156
77	1.03	1.84	0.31	1.96	1.28	0.40	1.53	158
66	2.05	0.33	0.07	0.37	1.69	0.34	1.84	171
72	2.07	1.33	0.13	1.31	1.70	0.24	1.76	179
76	2.07	1.84	0.31	1.96	1.58	0.41	1.82	176
85	3.04	1.84	0.31	1.96	1.90	0.33	2.03	136

Table III

ANALYSIS OF SOME TYPICAL BED RESIDUES FROM DEEP BED  
DESULFURIZATION AT 1600°F, 6 Atm.  $H_2$

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Wt. of Feed, gm	430 <sup>1)</sup>	860 <sup>1)</sup>	1720 <sup>2)</sup>
H	0.98	0.79	0.49
C	85.25	85.45	85.49
N	1.09	1.00	1.11
O	0.85	0.50	0.43
S	0.42	0.33	0.89
Ash	11.41	11.93	11.59

1) 60 Minutes treatment time.

2) 30 Minutes treatment time.

Table IV

SUMMARY OF DATA FROM DEEP BED DESULFURIZATION RUNS

Conditions: Pressure 6 Atm. Abs. Temperature 1600°F  
Inlet H<sub>2</sub> Rate 97.7 SCFH @ 70°F

Raw Feed Charged, gms	Bed Weight Grams		Hydrogen Treatment Time	Approx. Vol. H <sub>2</sub> /lb. Char SCF/Lb.	Sulfur Content of Residue		
	After Drying and Pretreatment, gms	Final			Organic	Sulfide	Total
500	430	416	30	50	0.34	0.14	0.50
500	430	411	60	100	0.29	0.13	0.42
500	430	405	120	200	0.12	0.07	0.19
1000	860	835	30	25	0.38	0.18	0.56
1000	860	822	60	50	0.23	0.10	0.33
1000	860	812	120	100	0.14	0.09	0.23
2000	1720	1671	30	12	0.47	0.42	0.89
2000	1720	1650	60	25	0.31	0.24	0.55
2000	1720	1633	120	50	0.21	0.12	0.33

Table V

APPROACH TO EQUILIBRIUM IN THE REMOVAL  
OF ORGANIC SULFUR FROM DISCO CHAR  
USING 25% H<sub>2</sub>-75% H<sub>2</sub>O FOR DESULFURIZATION AT 1600°F

<u>Initial Bed Weight, gms</u>	<u>Press. Atms. Abs.</u>	<u>Desulf. Time Mins.</u>	<u>Calculated % H<sub>2</sub>S in Effluent Hydrogen</u>	<u>Residue Organic S Content %</u>	
				<u>Experimental</u>	<u>Equilibrium</u>
20.8	1	81	0.17	0.80	0.40
38.8	1	93	0.29	0.93	0.61
80.8	1	109	0.43	1.01	0.79
34.5	6	37	0.12	0.49	0.28
69.5	6	22	0.39	0.97	0.76
69.7	6	48	0.17	0.54	0.40
107	6	25	0.49	0.95	0.86
107	6	57	0.25	0.58	0.54

Figure 1

FLOW DIAGRAM OF EXPERIMENTAL EQUIPMENT

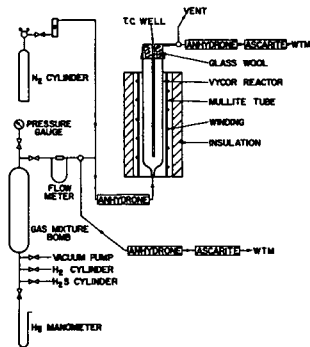


FIGURE 2  
TOTAL INHIBITION DATA AT 1350°F

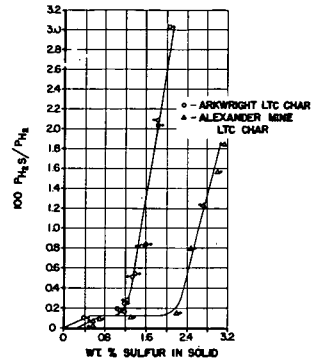


FIGURE 3  
TOTAL INHIBITION DATA ARKWRIGHT LTC CHAR

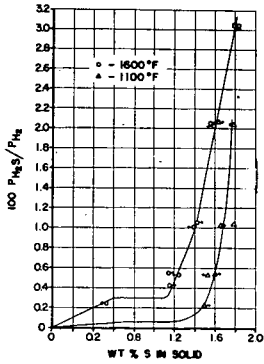


FIGURE 4  
TOTAL INHIBITION DATA FOR ORGANIC SULFUR

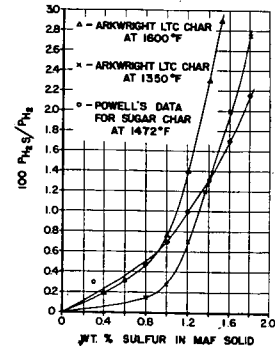


FIGURE 5  
EQUILIBRIUM CURVE FOR BATCH  
DESULFURIZATION COMPARISON  
WITH EXPERIMENTAL DATA

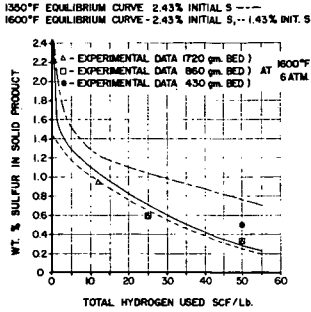


FIGURE 6  
SHALLOW BED DESULFURIZATION OF  
ARKWRIGHT CHAR

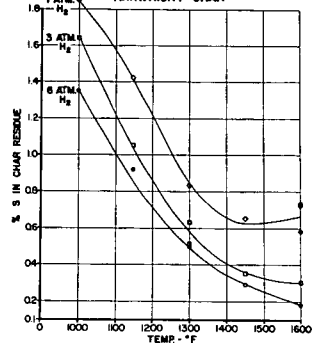


FIGURE 7  
SHALLOW BED DESULFURIZATION OF  
MONTGOMERY-10 CHAR

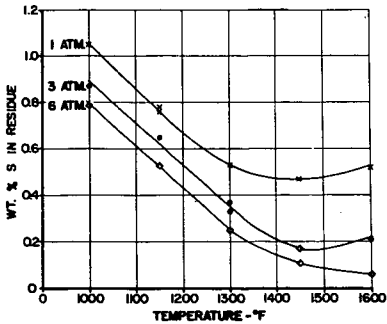


FIGURE 8  
DIFFERENTIAL DESULFURIZATION OF  
MOUNDSVILLE LTC CHAR

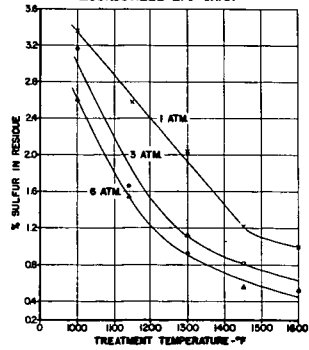




FIGURE 9  
SULFUR ELIMINATION OF THREE  
DIFFERENT LTC CHARS

